

## Photochemical Synthesis:† ( $\pm$ )- $\beta$ -Himachalene

By B. D. CHALLAND, G. KORNIS, G. L. LANGE, and P. DE MAYO\*

(*Department of Chemistry, University of Western Ontario, London, Ontario, Canada*)

THE sesquiterpene  $\beta$ -himachalene has been isolated from a number of sources, and its structure (IX) has been established by Dev<sup>1</sup> and by Erdtman<sup>2</sup> and their collaborators. We report here the synthesis of the racemic hydrocarbon (IX) and of himachalene dihydrochloride (X).

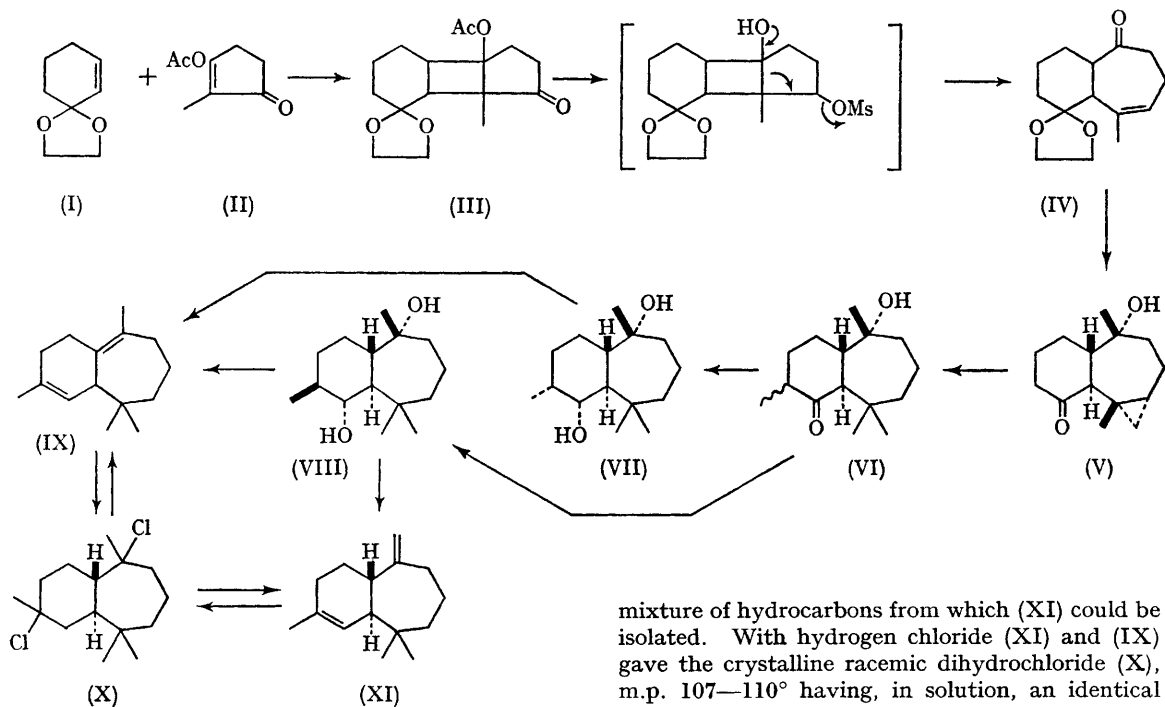
Irradiation of a solution of (I)<sup>3</sup> and (II)<sup>‡</sup> in cyclohexane solution gave the adduct (III). Reduction with sodium borohydride and conversion into the mesylate<sup>4</sup> followed by hydrolysis with 0.7% sodium hydroxide in aqueous dioxan gave (IV) in 35% yield based on (II).

Reaction of the ketal with methylmagnesium iodide, followed by treatment with the Simmons-Smith reagent<sup>5</sup> gave, after mild acidic hydrolysis, (V). Alkylation (methyl iodide-potassium t-butoxide in t-butyl alcohol-benzene) followed by hydrogenation of the product, in acetic acid solution containing sodium acetate, over a platinum-rhodium catalyst gave (VI).

Reduction of (VI) with sodium and alcohol, or with lithium aluminium hydride, gave a separable mixture of crystalline diols. Dehydration of two of these, (VII) and (VIII), with phosphorus

† Preceding Communication.

‡ We thank Dr. H. Smith, Wyeth Laboratories Inc., for a generous supply of 2-methylcyclopentane-1,3-dione.



oxychloride and pyridine gave a mixture from which, by gas-liquid chromatography, could be isolated (IX) identical with the naturally occurring hydrocarbon<sup>†</sup> in infrared spectrum, n.m.r. spectrum, and chromatographic behaviour. Dehydration of other diols gave, as did (VII) and (VIII), a

mixture of hydrocarbons from which (XI) could be isolated. With hydrogen chloride (XI) and (IX) gave the crystalline racemic dihydrochloride (X), m.p. 107—110° having, in solution, an identical infrared spectrum with that of the dihydrochloride derived from the natural hydrocarbon.<sup>§</sup> Treatment of (X) with pyridine afforded (XI) and (IX), thus providing a second route to (IX).

(Received, June 5th, 1967; Com. 559.)

§ We are very grateful to Professor H. Erdtman for specimens of pure  $\alpha$ - and  $\beta$ -himachalenes and to Dr. S. Dev for a generous sample of a mixture of  $\alpha$ - and  $\beta$ -himachalenes.

<sup>1</sup> T. C. Joseph and S. Dev, *Tetrahedron Letters*, 1961, 216.

<sup>2</sup> J. B.-Son Bredenberg and H. Erdtman, *Acta Chem. Scand.*, 1961, **15**, 685.

<sup>3</sup> H. W. Wanzlick, G. Collmer, and H. Milz, *Chem. Ber.*, 1955, **88**, 69.

<sup>4</sup> T. Durst, Thesis, University of Western Ontario, 1964.

<sup>5</sup> H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 4256.